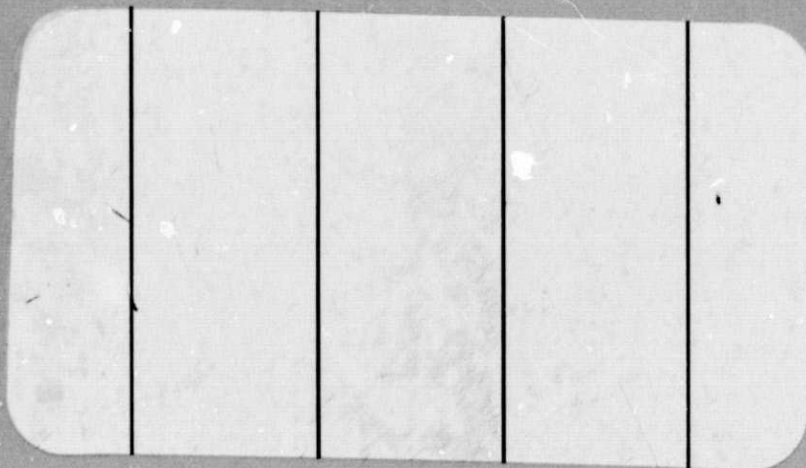


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National Aeronautics and Space
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SPACE STABLE THERMAL CONTROL COATINGS

1.0 INTRODUCTION

The potential that zinc orthotitanate possesses as a pigment for spacecraft thermal control applications has been thoroughly demonstrated in past studies at IITRI (Reference 1-3). The practical realization of this potential hinges most importantly on pigment stoichiometry and also on the production process and optimized preparative conditions associated with it. The "MOX" method, i.e., the use of zinc and titanium oxalate precursors, has the distinct advantages of simple and rapid processing, and of controlled pigment particle size.

The primary goals of this program for obtaining a specification quality zinc orthotitanate are:

- 1) Determination of the chemical identity of TiOX ("titanium oxalate").
- 2) Effect of Zn/Ti ratio for Zn_2TiO_4 on the reflectance spectra and stability to ultraviolet irradiation in vacuum.
- 3) Optimized processing parameters for reproducibly obtaining a pigment of the most desirable optical properties and behavior.

The ultimate goal of obtaining a specification thermal control coating appears well within achievable reality. The studies discussed in this report are designed to yield a Zn_2TiO_4 paint as an engineering material for use on future spacecraft.

During this reporting period, both pigment and paint studies were conducted. The effect of calcination conditions (temperature, time) on optical properties of Zn_2TiO_4 were determined. Paint studies were concerned with the effects of spraying technique, of pigment-to-binder ratio (PBR), and of thickness on the properties of finished coatings. The results are presented in the following sections.

2.0 PIGMENT STUDIES

The preparation of pigments remains an ongoing function on this program. This involves: 1) preparation of ZnCl_2 and TiCl_4 aqueous solutions; 2) reacting with oxalic acid to form the oxalate precursors; 3) dry ball milling of zinc oxalate with "TiOX" in a plastic media; 4) precalcination at $500^\circ\text{C}/2$ hrs; and 5) production of Zn_2TiO_4 using flash calcination at 900°C or 1050°C . Various pigments prepared during this report period are described in the following sections.

2.1 Low Temperature Synthesis: 600°C - 800°C

Pigments prepared by calcination at 600°C - 800°C were evaluated during this period. These low temperature syntheses were conducted to determine: 1) extent of $\text{ZnO} + \text{TiO}_2$ reaction as indicated by R_{350} ; and 2) the potential of higher peak reflectance with finer particle size powder obtained at these lower temperatures. The data tabulated in Table I and graphically represented in Figure 1 show relatively low R_{350} values which increase as a function of both temperature and reaction time. The highest R_{350} values was shown by the $800^\circ\text{C}/16$ hrs material; however, this value was lower than any comparable 2.0 Zn/1.0 Ti powders calcined at 900°C .

The peak reflectance (R_{500}) values were not significantly higher than those for 900°C calcined pigments. Based on these results, the use of a calcination temperature lower than 900°C

TABLE I

REFLECTANCE OF Zn_2TiO_4 POWDERS SYNTHESIZED AT $600^\circ - 800^\circ$

(Zn/Ti RATIO = 2.0/1.0)

Temp, °C	CALCINATION CONDITIONS		R_λ		$R_{350}/R_{500} \times 100$
	Time, hrs.	350	500	1000	
600	8	15.0	97.0	97.5	15.5
	16	23.0	94.5	99.0	24.3
700	8	-----	-----	98.5	-----
	16	43.5	91.0	98.5	47.8
800	2	38.0	94.5	96.0	40.2
	8	47.0	96.0	96.0	49.0
	16	53.5	94.5	96.0	56.6

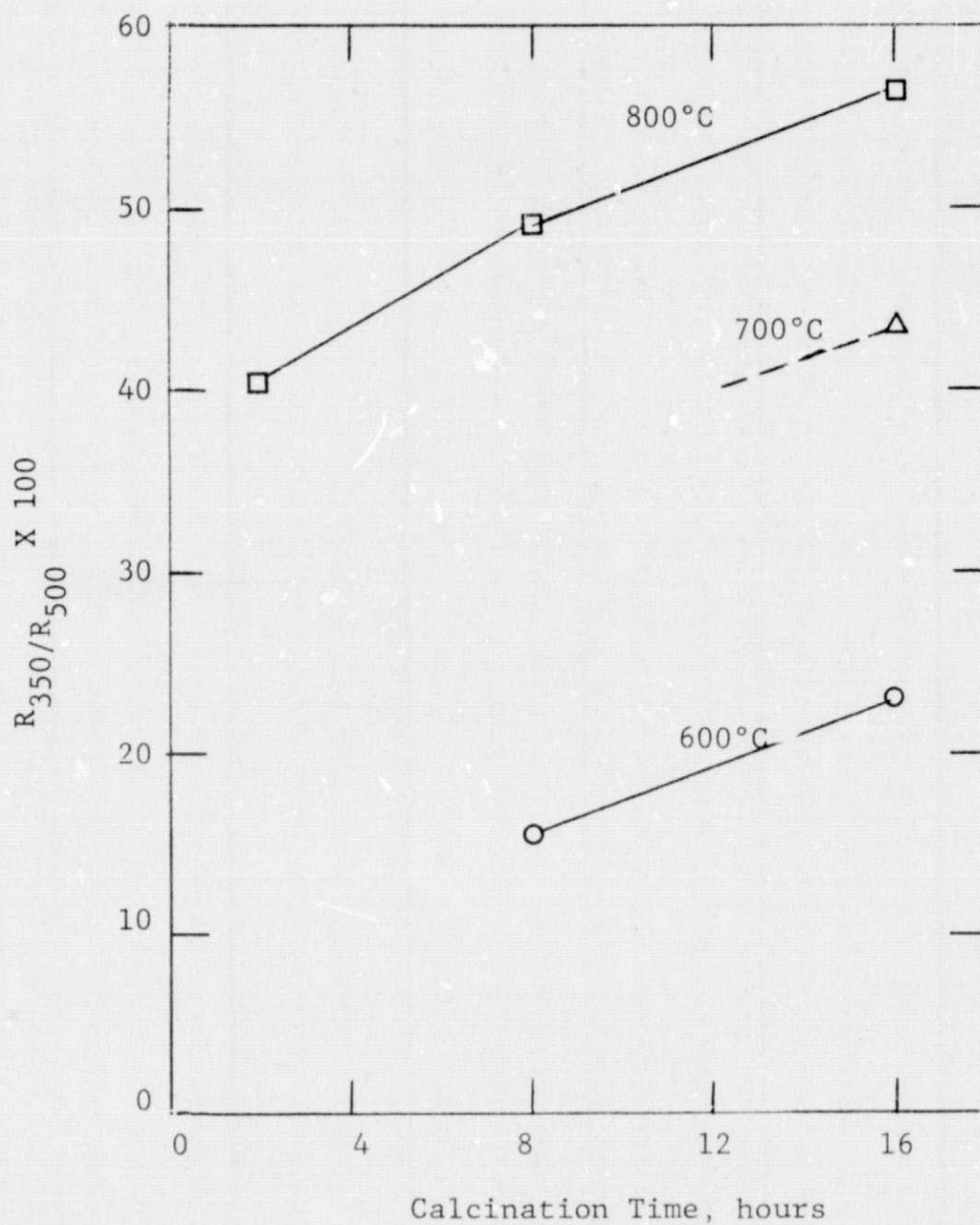


Figure 1. REFLECTANCE AT 350 nm vs. CALCINATION TIME FOR Zn_2TiO_4 POWDERS PREPARED AT 600°C-800°C

to obtain Zn_2TiO_4 , does not appear warranted.

2.2 Zn_2TiO_4 Synthesis at 900°C

A series of Zn_2TiO_4 powders were prepared by calcination at 900°C for time periods of from 1 to 16 hours.

Representative reflectance values for these powders are presented in Table II, and graphical representation of the R_{350} values is shown in Figure 2. The R_{350} , or "knee" reflectance, may be used to show the amount of free ZnO in the powders, i.e., lower values indicate greater amounts of ZnO.

It was anticipated that lesser amounts of ZnO would be observed after longer calcination times which would favor completeness of reaction. However, no such trend was shown at any of the stoichiometry levels. A puzzling aspect is that for the 1.95 and 2.00 Zn/Ti ratio materials, the R_{350} values suggest an increase in ZnO content with longer calcination times. These results indicate that the $\text{ZnO} + \text{TiO}_2$ reaction is essentially complete after one hour at a 900°C calcination temperature. The anomalous trend in R_{350} values as a function of hold time at 900°C will be re-evaluated as time and funds permit.

Another relationship shown in this study is R_{350} vs Zn/Ti ratio. The R_{350} values were the highest at a 1.85 Zn/Ti ratio, with decreasing values at higher Zn/Ti ratios. This trend agrees with previous data of stoichiometry vs R_{350} .

A final observation is that the peak reflectance values at 500 nm were all quite high, indicating a potential for low α_s . The high reflectance also extends to the infrared wavelengths (note R_{1000} in Table II). Reflectances of greater than 95% at 2000 nm were observed for several of these samples.

TABLE II

REFLECTANCE OF Zn_2TiO_4 POWDERS AS A
FUNCTION OF STOICHIOMETRY AND CALCINATION TIME AT 900°C

SAMPLE DESCRIPTION		R_λ			R_{350}/R_{500}	X 100
		350	500	1000		
Zn/Ti Ratio	Hold Time at 900°C, hrs.					
1.85	1	81.0	97.0	96.0	83.5	
	2	83.0	96.0	98.0	86.5	
	4	82.0	96.0	98.0	85.4	
	8	76.0	90.5	96.0	84.0	
	16	82.0	97.0	98.0	84.5	
1.90	1	80.0	96.0	99.0	83.3	
	2	75.0	95.5	96.0	78.5	
	4	----	----	96.0	----	
	8	76.0	93.0	96.0	81.7	
	16	76.0	96.0	97.0	79.2	
1.95	1	65.0	94.5	96.0	68.8	
	2	68.0	97.0	99.0	70.1	
	4	69.0	98.0	96.5	70.4	
	8	62.0	96.0	96.0	64.6	
	16	54.0	96.5	97.0	56.0	

TABLE II (Cont'd)

REFLECTANCE OF Zn_2TiO_4 POWDERS AS A
FUNCTION OF STOICHIOMETRY AND CALCINATION TIME AT 900°C

SAMPLE DESCRIPTION		R_λ			$R_{350}/R_{500} \times 100$
		350	500	1000	
Zn/Ti Ratio	Hold Time at 900°C, hrs.				
2.00	1	65.0	98.0	99.0	66.3
	2	62.0	96.0	96.0	64.6
	4	57.0	93.5	95.0	61.0
	8	51.0	94.5	94.0	54.0
	16	59.0	93.0	96.0	63.4
2.05	1	60.0	97.0	98.5	61.9
	2	58.0	97.0	98.5	59.8
	4	57.0	97.0	98.5	58.5
	8	56.0	97.0	98.5	57.7
	16	57.0	97.0	99.0	58.8

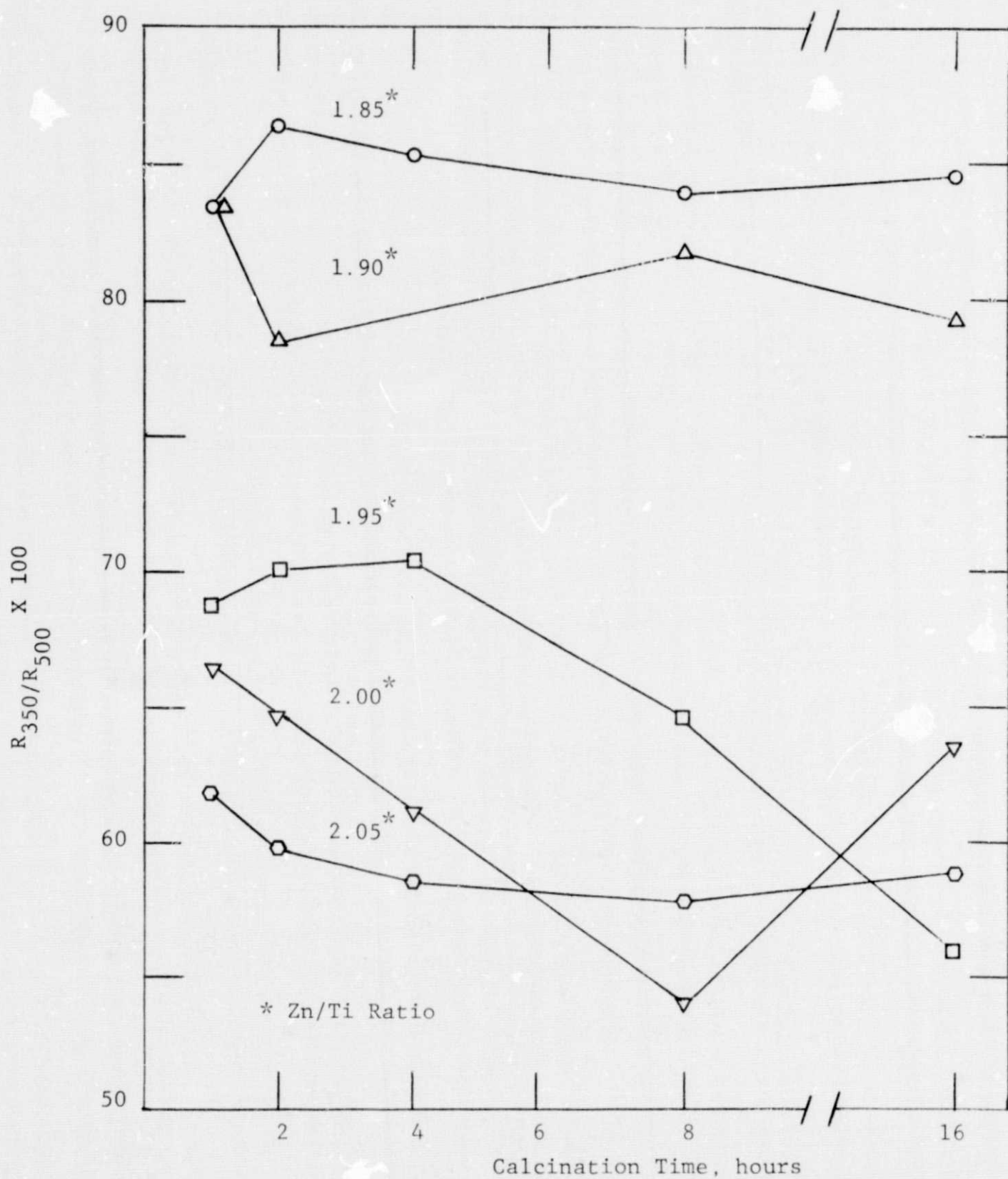


FIGURE 2. REFLECTANCE AT 350 nm vs CALCINATION TIME FOR Zn_2TiO_4 POWDERS PREPARED AT 900°C

3.0 PAINT STUDIES

In the current studies to obtain a highly reflective and stable Zn_2TiO_4 pigment thermal control coating, an inorganic silicate vehicle (as opposed to a polymeric silicone binder) has been chosen for prime consideration. This choice is due to several desirable characteristics of silicate coatings: 1) lower solar absorptance, α_s ; 2) higher emittance, ϵ ; 3) greater stability in UV-vacuum; 4) no outgassing problems; and 5) higher electrical conductivity, minimizing charge buildup problems.

Historically, the objections to a silicate-bonded coating have been based on two disadvantages; 1) difficulties in spray technique to achieve a flaw-free, well-bonded coating; and 2) difficulty in cleanability. However, the use of Z93 (silicate-bonded ZnO) on large areas of the Gemini early in the space program attests to its applicability. The cleanability problem may be circumvented through the use of protective polymeric films. Studies (Ref. 4) at IITRI have shown that storage under plastics such as Mylar, Lexan, Type A Teflon, and Tedlar for periods up to 14 months maintains the excellent stability of Z93 to UV-vacuum.

3.1 Sample Preparation

Paint formulations were prepared by ball-milling of pigment - PS7 potassium silicate - distilled water mixtures of varying PBR for 6 hours. Coatings were applied by conventional spray painting techniques and cured in air at room temperature. Samples were prepared on both IITRI and MSFC paint coupons for evaluation at both facilities.

Initial compositions which were used are listed in Table III. These are similar in total liquid content to Z93. In the preparation of samples by the spray technique, Z93 (silicate-bonded

TABLE III
PAINT COMPOSITIONS FOR
SPRAYING STUDIES

<u>COMPONENT</u>	<u>PIGMENT TO BINDER RATIO (PBR)</u>		
	<u>5.32</u>	<u>6.08</u>	<u>7.09</u>
Zn_2TiO_4	40 gms	20 gms	20 gms
PS7(potassium silicate)	16 cc	7 cc	6 cc
H_2O	24 cc	13 cc	14 cc

TABLE IV
PAINT COMPOSITIONS: DRY SPRAY MIXTURES

<u>COMPONENT</u>	<u>PIGMENT TO BINDER RATIO (PBR)</u>		
	<u>4.26</u>	<u>5.32</u>	<u>7.09</u>
Zn_2TiO_4	20 gms	20 gms	20 gms
PS7(potassium silicate)	10 cc	8 cc	6 cc
H_2O	7 cc	8 cc	10 cc

ZnO) samples were also prepared for comparison. Two differences were observed between Zn_2TiO_4 paints and Z93: 1) Zn_2TiO_4 compositions appeared to go on much "wetter" than did Z93; and 2) for the same number of spray cycles, better thickness buildup was achieved with A93.

The first difference was probably due to an excess of water content in the Zn_2TiO_4 mixtures. The Zn_2TiO_4 powder is coarser than calcined SP-500 ZnO and requires less water to achieve a sprayable viscosity. The second difference may also be traceable to the excess water in the Zn_2TiO_4 mixtures. The "wet" appearance which signals the end of a spray cycle was achieved more rapidly with Zn_2TiO_4 , resulting in a lesser amount of coating per spray cycle. Thus, a decrease in water content plus modification of spray technique were indicated as requirements to achieve coating thickness buildup with Zn_2TiO_4 -silicate paints.

Additional studies involved compositions of lesser liquid content as listed in Table IV. Improved sprayability was shown by these compositions, and an even lower water content appears feasible.

3.2 Evaluation of Coatings

A plot of coating thickness vs coating weight for compositions in Table III is shown in Figure 3. There appears to be a good linear correlation for the 5.32 PBR samples which represent the bulk of the data. The limited data for 6.08 and 7.09 PBR samples also fall on this curve, indicating no significant change in coating density with increasing PBR.

Selected reflectance values for these paints as a function of thickness are shown graphically in Figure 4. The following observations can be made from these data:

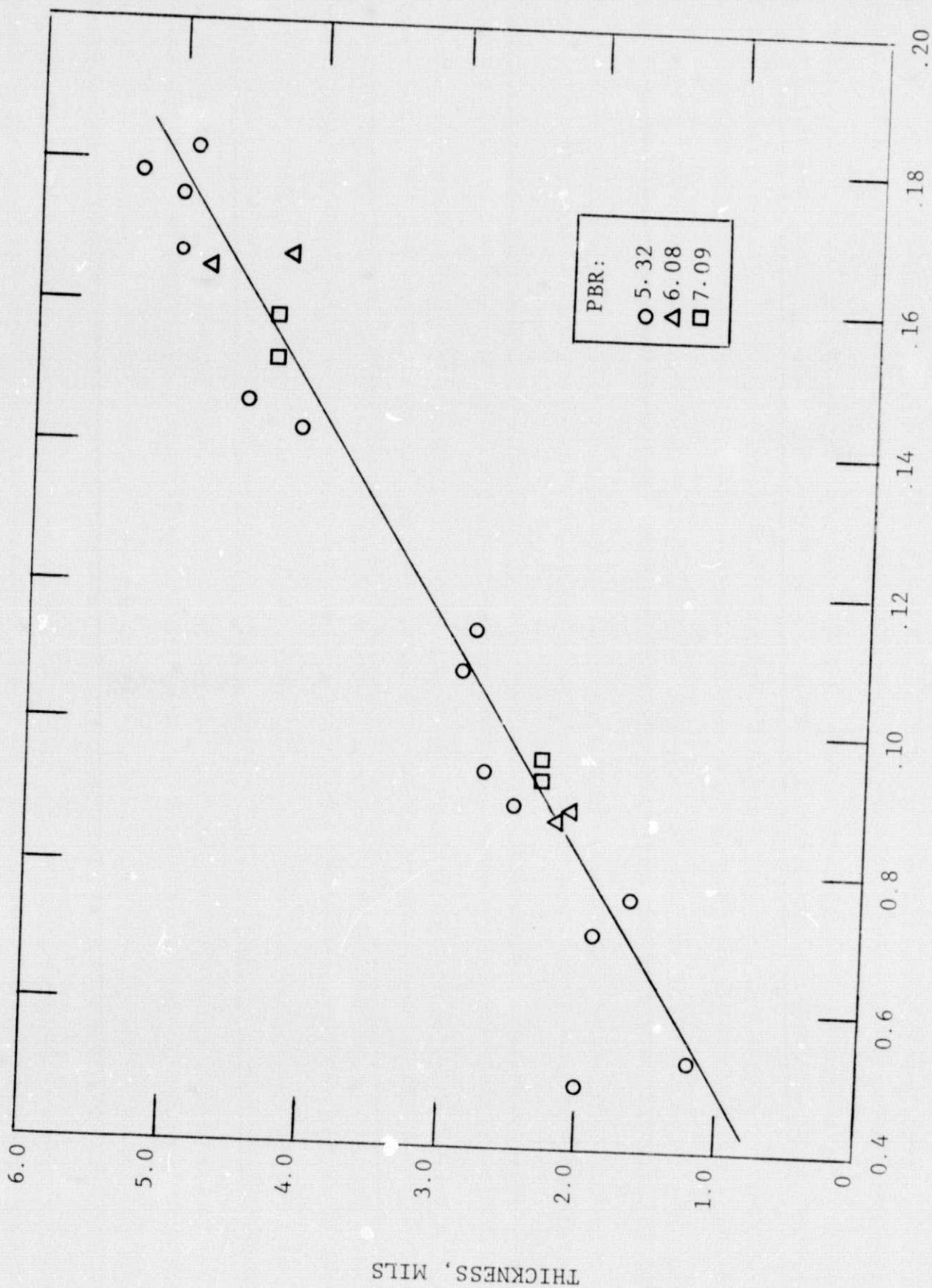


Figure 3. COATING THICKNESS VS WEIGHT for $\text{Zn}_2\text{TiO}_4^*$ -SILICATE COATINGS
 (* $1050^\circ\text{C}/2\text{hrs}$, $\text{Zn}/\text{Ti} = 2.05$)

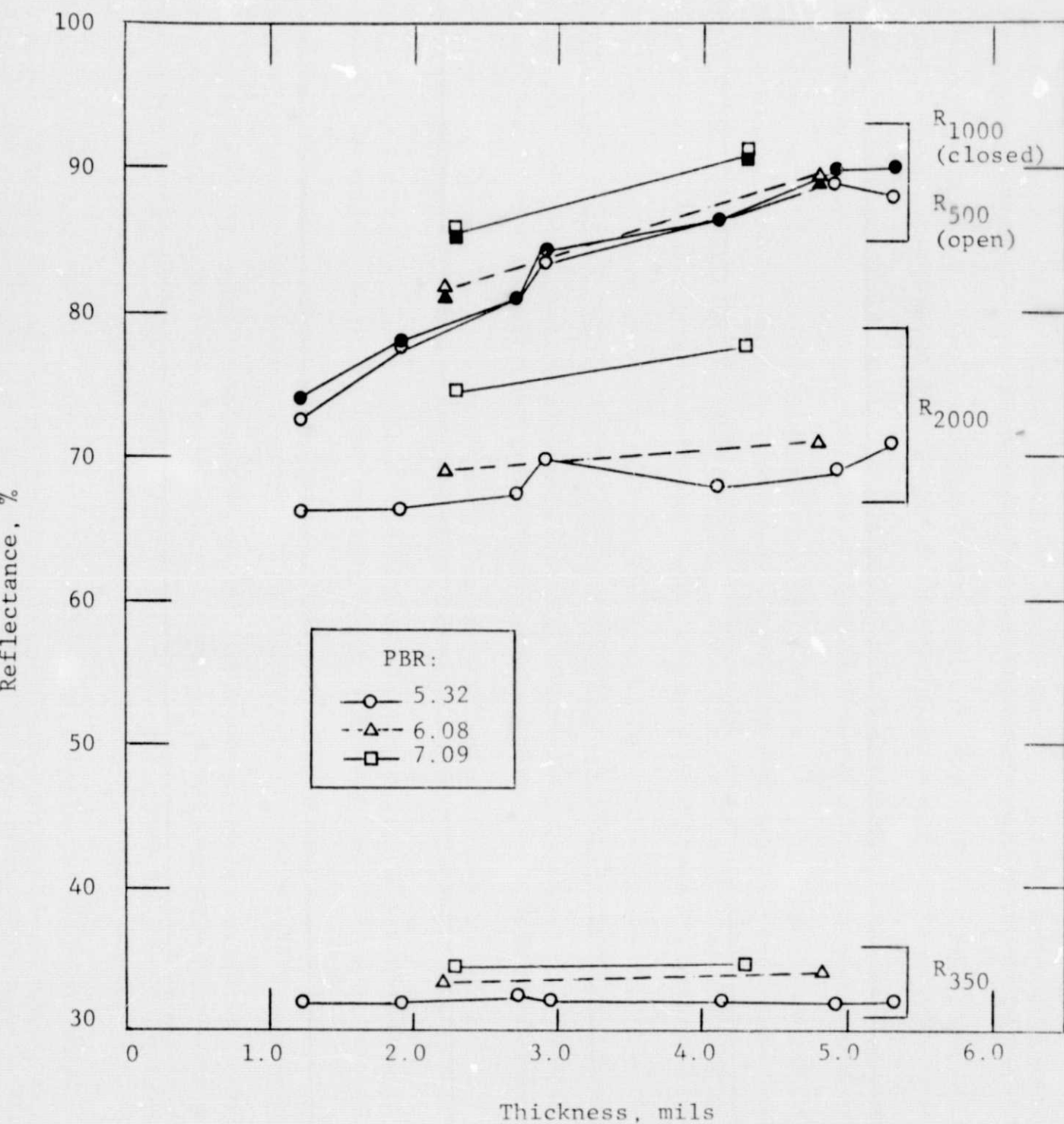


Figure 4. REFLECTANCE VS COATING THICKNESS FOR $Zn_2TiO_4^*$ -SILICATE COATINGS (*1050°C/ 2 HRS, Zn/Ti = 2.05)

1. At wavelengths of 500, 1000, and 2000 nm there is an increase in reflectance with increasing thickness.
2. At 350 nm, thickness does not appear to have an effect on reflectance.
3. An increase in reflectance at the various wavelengths is shown with increasing PBR.

A significant finding in these studies was the ability to increase the PBR to 7.09 while retaining good physical integrity in the coating. This is much higher than the 4.26 PBR which was determined to be optimum for Z93, and may be attributed to lesser binder demands by the coarser Zn_2TiO_4 . This is advantageous in two respects: 1) a higher reflectance can be achieved; and 2) greater stability in a UV-vacuum environment may be achieved.

3.3 UV-Vacuum Studies

Paint samples with the compositions listed in Table IV were prepared using Zn_2TiO_4 pigments with Zn/Ti ratio of 1.95 and 2.00, calcined at 900°C and 1050°C. Coatings on MSFC coupons have been submitted to MSFC and are now undergoing UV-vacuum testing. Paint samples on IITRI coupons are being evaluated for their physical and optical characteristics. A preliminary result which appears quite encouraging is that 7 mil coatings of 7.09 PBR exhibit an α_s of 0.13. Elimination of the ZnO "knee" should lower this value to 0.11.

4.0 SUMMARY

Silicate paints pigmented with Zn_2TiO_4 have been shown to exhibit different characteristics as compared to that pigmented with ZnO (Z93). A higher pigment loading of 7.09 PBR vs 4.26

PBR (Z93) is possible with the coarser Zn_2TiO_4 . Maximum reflectance is achieved at a 5 mil thickness for Z93; Zn_2TiO_4 paints require at least a 7 mil buildup to reach this maximum. To date, an α_s of 0.13 has been achieved with a clear potential of 0.11 with removal of free ZnO. Tests are now underway to examine the effect of a high pigment concentration on UV-vacuum stability.

Personnel who have contributed to this work include J. E. Brzuskiwicz, Jr., J. E. Gilligan, and W. R. Logan.

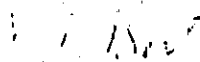
Respectfully submitted,

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